

SOME NOVEL REACTIONS OF CONDENSED AZOLE DERIVATIVES WITH DIMETHYL  
ACETYLENEDICARBOXYLATE

Norio Kawahara and Takako Nakajima

Hokkaido Institute of Pharmaceutical Sciences,

7-1, Katsuraoka-cho, Otaru, Hokkaido, 047-02, Japan

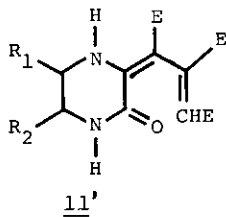
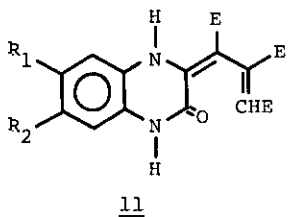
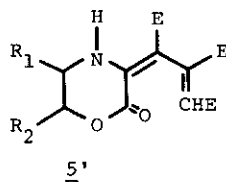
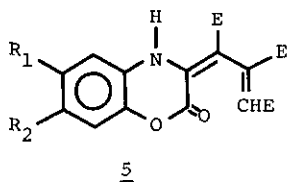
Tsuneo Itoh, Hiroaki Takayanagi and Haruo Ogura

School of Pharmaceutical Sciences, Kitasato University,

Minato-ku, Tokyo 108, Japan

We obtained new results on treating of benzoxazole derivatives with dimethyl acetylenedicarboxylate (DMAD) in alcohols at room temperature and discussed plausible mechanisms for these addition reactions.

- 1) Benzoxazole derivatives (1) and DMAD gave 1 : 1 : 1 adduct (2, solvent adduct), 1 : 1 : 1 adduct (3, H<sub>2</sub>O adduct) and a ring opened compound (4). The structure of another addition product was elucidated to be (5) by spectral data and X-ray analysis.
- 2) 2-Alkylbenzoxazole derivatives (6) and DMAD gave 1 : 1 : 1 adduct (7, H<sub>2</sub>O adduct), a ring opened compound (8), a compound containing seven membered ring (9) and 1 : 1 : 1 adduct (10, solvent adduct).
- 3) We could easily prepare 5 and 5' by heating of aminophenol derivatives or amino-alcohols with excess volume of DMAD in dioxane. Furthermore, we could prepare 11 and 11' by treating of o-phenylenediamine derivatives or diamines in similar conditions. Compound (11) was heated by refluxing in DMSO to give a novel tricyclic compound (12).



E = COOCH<sub>3</sub>